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KINETICS OF HYDROLYSIS AND PRODUCTS OF HYDROLYSIS AND PHOTOLYSIS OF TETRYL

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RESEARCH AND TECHNOLOGY DEPARTMENT

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Tetryl	Tetryl Hydrolysis Products
Tetryl Hydrolysis	Tetryl Photolysis Products

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This study involved the determination of tetryl hydrolysis kinetics in buffered aqueous solutions at $40°$, $72°$, and $85°$C, and the identification and quantification of the major products of both the light and dark hydrolysis reactions of tetryl. The kinetic data indicated a first order disappearance of tetryl for the buffered aqueous solutions at $40°$, $72°$, and $85°$C, and a first order dependence on OH^- ion at $40°$C. The environmental hydrolysis ($20°$C and pH 6.8) half life of tetryl ($t_{1/2} \simeq 302 \pm 76$ days) could only be

20. (Cont.)

estimated for a range of activation energies. The major components isolated from the hydrolysis study included: picrate ion, N-methylpicramide, methylnitramine, nitrate ion, and nitrite ion. Several other compounds were also formed but were not identified.

FOREWORD

Since tetryl has been found as a soil contaminant associated with past Army manufacturing operations, it was necessary to determine its environmental half life and hydrolysis products to ascertain if additional clean-up procedures are necessary.

This work was funded by the U.S. Army Toxic and Hazardous Material Agency, under the direction of the U.S. Army Medical Research and Development Command (D. Rosenblatt - Project Officer, Work Unit Number 6.27.04A AF25).

This report presents data on the environmental half life of tetryl and also identifies and quantifies its major hydrolysis products.

Approved by:

J. F. PROCTOR, Head
Energetic Materials Division

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INTRODUCTION

N,2,4,6-tetranitro-N-methylaniline (tetryl) has been used as an explosive ingredient since 1906, both in booster and main charge explosive compositions. However, in more recent systems, it is being replaced by compositions containing RDX and HMX.[1] Tetryl has been found as a soil contaminant associated with past Army manufacturing operations,[2,3] and is reported to be soluble in fresh water to the extent of 75 ppm (20°C)[4] and in seawater to the extent of 25 ppm (25°C).[5] It is also toxic with a particularly detrimental effect on the skin.[6]

Several researchers have reported[7] that tetryl hydrolyzes in mild base to picrate ion, methylamine, and nitrite ion. Methylnitramine formation is also a possibility, and due to its stability in water the latter could act as a methylating agent. Because of this stability, methylnitramine may also be a potential cause of "frame shift" mutations, although its mutagenicity has not as yet been determined. John Hoffsommer has reported on the slow hydrolysis of saturated tetryl solutions (~ 25 ppm) in seawater (pH ~ 8.1). He observed an 88 percent conversion to picric acid in 101 days at 25°C in low actinic glassware. The formation of picric acid by spectrographic measurement (λ = 352 nm, ε = 14,130)[8] was in agreement with the decrease noted in tetryl concentration by GC analysis.* However, Hoffsommer suggested that biodegradation in the seawater samples was also probable.

In considering the environmental fate of tetryl in soil and groundwater, several reactions have to be considered since it is susceptible to at least three major pathways of degradation or decomposition: (1) photolysis, (2) biodegradation, and (3) hydrolysis. For this reason, the following reactions and kinetic studies were undertaken:

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*GC analysis of tetryl can be misleading due to thermal decomposition of tetryl in the GC injection port forming N-methlypicramide and another unidentified product.

o   A light hydrolysis* reaction over a period of 20 days at ambient temperature.

o   Dark hydrolysis** reactions for periods of 20 and 90 days at ambient temperature.

o   A borax buffered dark hydrolysis reaction over a 90-day period at ambient temperature.

o   Tetryl hydrolysis kinetics in buffered aqueous solutions (pH range 4 to 9) at 40°, 72°, and 85°C.

From the above studies, the major products of both light and dark tetryl hydrolysis reactions were identified and quantified. The kinetic data should allow the determination of a pH versus rate profile of tetryl, as well as the calculation of activation energies in order to predict hydrolysis half lives at environmental conditions (20°C and pH 6.8).

EXPERIMENTAL

PROCEDURE

Light and Dark Hydrolysis

Two solutions of tetryl were prepared in distilled water (12 mg/L). One was placed in the dark for 20 days while the other remained on the laboratory bench top in room light, both were stored at ambient temperature. The dark hydrolysis reaction was repeated with tetryl solutions (15 mg/L) in (1) 0.005 M borax buffer and (2) distilled water. The water solution was placed in the dark while the borax solution was placed in low actinic glassware on the laboratory bench top. Both solutions were again stored at ambient temperature.

Tetryl Hydrolysis Kinetics

The tetryl hydrolysis kinetics were determined in buffered aqueous solutions which were shielded from light. Reactions were carried out in 100 ml stoppered volumetric flasks submerged in constant-temperature baths maintained at 40°, 72°, and 85°C. Initial tetryl concentrations ranged from 1 to 20 mg/L. Two types of baths were used: (1) a Braun Thermomix 1460, 3-gallon, 1,000-watt unit, with ±0.01 temperature stability; and (2) a modified Sargent

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*Light hydrolysis--a hydrolysis reaction under ambient lighting conditions.

**Dark hydrolysis--a hydrolysis reaction shielded from light.

Welch Termoniter unit with 1,500 watts of proportional heating elements in a 16-gallon American Instrument Company Constant Temperature Bath with ±0.01°C temperature stability. The NBS-calibrated thermometers were readable to ±0.02°C. The samples were exposed to light only while cooling, prior to analysis.

MATERIALS, REAGENTS, AND pH DETERMINATIONS

For the majority of the kinetic runs, three NBS standard buffers were used. They were 0.01 M potassium acid phthalate (KHPhth) for pH 4; equivalent moles of KH_2PO_4/Na_2HPO_4 (0.005, 0.025, 0.05 M for each) for pH 6.8; and 0.01 M $Na_2B_4O_7 \cdot 10\ H_2O$ for pH 9.18. The actual pH value was measured at each temperature (40°, 72°, and 85°C) to allow an exact calculation of hydroxide concentration. A model number 130 Corning pH meter and a Corning Ag/AgCl combination electrode (#476115) with an accuracy of ±0.001 pH units were used.

The pH meter was calibrated at ambient temperature with the appropriate NBS buffer standard. Twenty-five ml samples of the kinetic stock solutions were added to a small (50 ml) insulated constant temperature bath which contained the combination electrode and thermometer. The solutions, electrode, and thermometer were allowed to equilibrate for 20 minutes after the thermometer had reached temperature before a pH reading was taken. The system was sealed to prevent evaporation. Since most of the kinetic stock solutions were made up with NBS buffers to standard concentrations, values were checked against the standard pH tables. Our pH measurements were within 0.03 units of those reported.

The samples of tetryl, picric acid, and N-methylpicramide used for this study were supplied by John Hoffsommer of this Center and were determined to be 99 percent pure by LC and TLC analyses. Samples of methylnitramine were obtained from George Nauflett, also of this Center.

TETRYL ANALYSIS

The disappearance of tetryl was monitored via LC using a Waters ALC-440/202 instrument with a U-6K injector and an isocratic 50/50, v/v methanol/water solvent system. Flow rates were 2 ml/minute and detection was by a Waters Model 440 UV detector fixed at $\lambda = 254$ nm.

A Whatman stainless steel LC column, 4.6 mm ID x 25 cm x 1/4 inch, and packed with 10 μm C18-ODS reverse phase material was used. Tetryl concentrations were measured by comparison of integrated peak areas from the kinetic runs with calibrated external injections of known amounts of tetryl from a stock solution. The stock solution was freshly prepared for each run, kept in the dark, and refrigerated during each experiment. Twenty-five to fifty μl samples were removed at regular intervals from the reaction solution and injected directly into the LC, preceded and followed by the standard tetryl injection.

PRODUCT ANALYSIS

The hydrolysis products of tetryl were identified by comparison of their LC retention times with those of authentic samples. This was verified by determining retention times on two different column support phases and in two different solvents: (1) a Whatman Reverse Phase C18 column, 4.6 nm ID x 25 cm x 1/4 inch, with 50:50 methanol/water, v/v (Figure 1), and (2) a Hewlett Packard 10 μm RP-8, 4.6 mm x 25 cm column with 50:50 methanol/water, v/v, containing 5×10^{-3} M tetrabutyl ammonium phosphate and buffered at pH 7.5 (Pic-A reagent) (Figure 2). The latter column/solvent system is effective in increasing the retention time for picric acid (ion-pair liquid chromatography).[9] Nitrate and nitrite ions were also determined on a Dionex Ion Chromatograph Model 10, using as eluent a mixture of 3×10^{-3} M sodium bicarbonate and 2.4×10^{-3} M sodium carbonate. One milliliter samples were removed from the kinetic runs and injected directly into the IC, preceded and followed by injections of standard NO_2^- and NO_3^- solutions.

RESULTS AND DISCUSSION

LIGHT AND DARK HYDROLYSIS

The retention times and relative response factors of tetryl and its hydrolysis products are listed in Table 1. The results of the LC and IC analyses of the light and dark hydrolysis reaction solutions can be found in Table 2. From the data obtained in this cursory product study, it is obvious that tetryl photolyzes under ambient lighting conditions at least an order of magnitude faster than it hydrolyzes. The major detectable photoproduct is N-methylpicramide. Tetryl also reacts in concentrated sulfuric acid to form N-methylpicramide (trinitromethylaniline). This reaction proceeds fairly rapidly at elevated temperatures (e.g., 60°C and above) but slowly at ambient temperature.[7] The principal detectable product of the dark hydrolysis reaction in borax buffer is methylnitramine. Other identified products include: picrate ion, nitrite ion, N-methylpicramide, and nitrate ion. Several additional compounds were also formed but were not identified. The dark hydrolysis reaction in borax buffer was continued for an extra 20 days after the initial 90-day period to determine the decomposition product or products of the methylnitramine, however, no degradation of the methylnitramine was noted. Under the above photolysis conditions tetryl reacts faster than it does under environmental conditions of 40°C and a pH of 6.88 ($t_{1/2}$ = 63 days, see Table 3).

TETRYL KINETICS

Each tetryl hydrolysis in buffered aqueous solution followed simple pseudo first-order kinetics with respect to tetryl concentration. Several runs at 40°, 72°, and 85°C indicated good first-order log conc. versus time plots for over 300-fold changes in tetryl concentration (> 99 percent disappearance). Some runs at 40°C required over 3 months for collection of data whereas at pH 9 and

HPLC CONDITIONS
SOLVENT: METHANOL:WATER
        (50:50, V/V)
FLOW RATE: 2 ML/MINUTE
UV DETECTOR: 254 NM
COLUMN: WATERS C-18 REVERSE PHASE
CHART SPEED: 2 CM/MINUTE

T = 0 MINUTES

T = 25 MINUTES AT
    85°C AND pH = 9
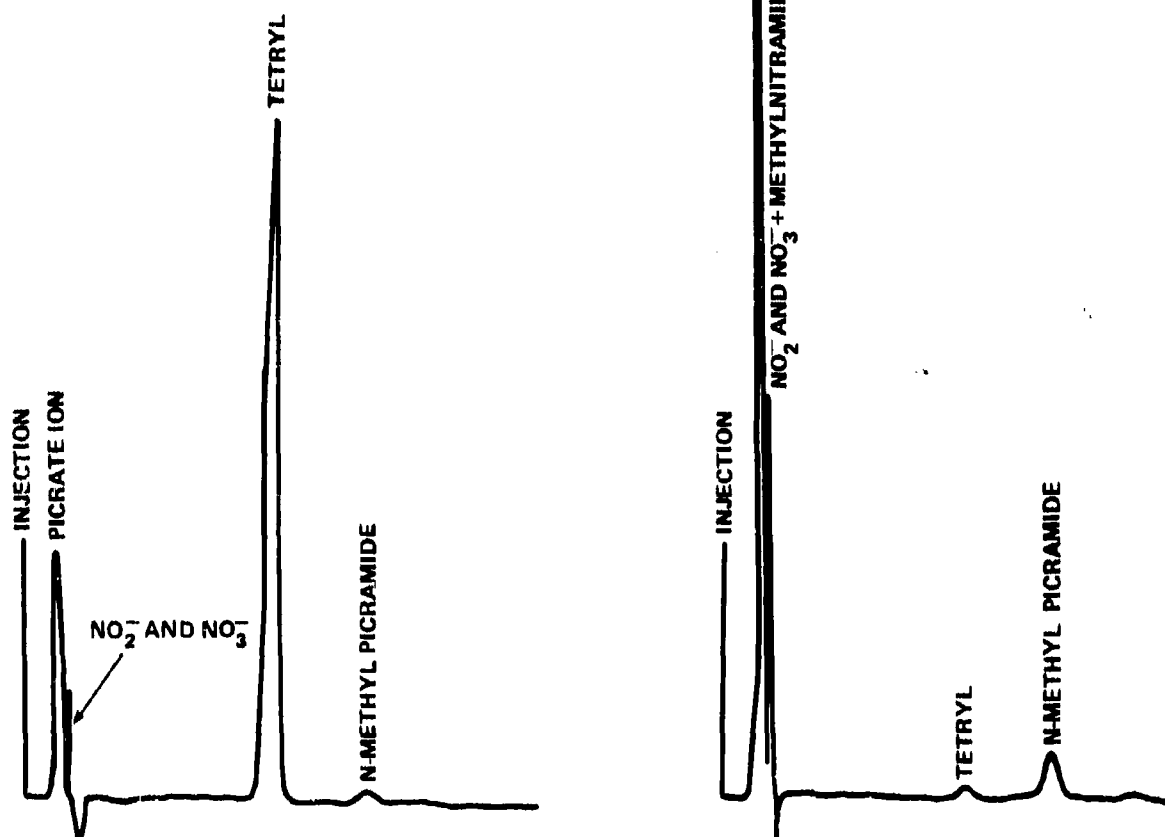
FIGURE 1. HPLC CHROMATOGRAMS OF AQUEOUS TETRYL IN 0.01M BORAX BUFFER, AT pH 9.0

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HPLC CONDITIONS
SOLVENT: METHANOL: WATER
(50:50, V/V) WITH PIC-A REAGENT
FLOW RATE: 2 ML/MINUTE
UV DETECTION: 254 NM
HP-C$_8$ REVERSE PHASE
CHART SPEED: 2 CM/MINUTE
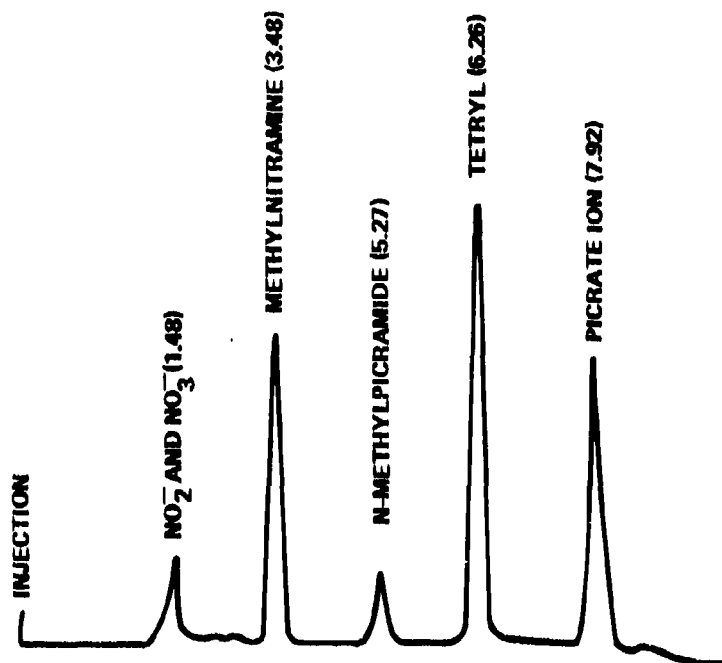
FIGURE 2. HPLC CHROMATOGRAM OF STANDARD METHYLNITRAMINE, N-METHYLPICRAMIDE, TETRYL, AND PICRATE ION SOLUTION USING PIC-A REAGENT

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TABLE 1. LC RETENTION TIMES AND RELATIVE RESPONSES FOR TETRYL
AND ITS HYDROLYSIS PRODUCTS

COMPOUND	RETENTION TIMES (MIN)		RELATIVE RESPONSE (WATERS)* AT 254 nm
	WATERS*	HEWLETT PACKARD**	
Tetryl	6.21	6.26	1.0
Picrate Ion	0.95	7.92	8.3
N-Methylpicramide	8.63	5.27	0.83
Methylnitramine	0.98	3.48	~0.60
NO_2^-	1.08	1.50	~0.002
NO_3^-	1.06	1.48	~0.001

*Waters C18 Reverse Phase C18-ODS, 50:50 methanol/water, flow rate: 2 ml/minute, UV detector: 254 mm.

**Hewlett Packard 10 μm RP-8, 50:50 methanol/water with 5×10^{-3} M tetrabutyl ammonium phosphate buffered at pH 7.5 (Pic-A reagent), flow rate: 2 ml/minute, UV detector: 254 mm.

TABLE 2. TETRYL HYDROLYSIS PRODUCTS

HYDROLYSIS REACTION	% TETRYL REACTED	REACTION TIME/MEDIUM	WEIGHT % OF PRODUCTS FORMED					INITIAL pH	FINAL pH
			PICRATE ION	NO_2^-	NO_3^-	METHYL-NITRAMINE	N-METHYLPICRAMIDE		
Dark	3.2	20/H_2O	~2.3	← ~0.01 →		← →	< 1.0	5.95	6.10
Light	95.4*	20/H_2O	~3.9	9.4	35.2	0.01	41.0	5.95	4.25
Dark	5.1	90/H_2O	~3.4	← 0.3 →		← →	1.0	6.10	5.04
Dark	98.7*	90/0.005 M borax-H_2O	28.5	4.1	3.1	66.0	4.1	8.90	8.80

*Several other compounds were formed which were not identified

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TABLE 3. KINETIC DATA FOR HYDROLYSIS OF TETRYL IN
BUFFERED AQUEOUS SOLUTIONS

TEMP (°C)	pH (± 0.01)	BUFFER	NO. POINTS	k_{obs} (hr^{-1}) x 10^{-4}	CORRELATION COEFFICIENT[10]
40	6.88	0.05 M PO_4	9	4.53 ± .21	0.999
40	6.88	0.05 M PO_4	8	4.93 ± .38	0.997
40	8.94	0.005 M Borax	6	446 ± 12	0.999
40	8.96	0.001 M Borax	4	388 ± 7	0.999
40	8.96	0.005 M Borax	6	437 ± 12	0.999
72	4.13	0.005 M KHPhth	6	2.01 ± .14	0.999
72	4.13	0.01 M KHPhth	6	2.43 ± .19	0.998
72	6.87	0.05 M PO_4	6	401 ± 10	0.999
72	6.87	0.05 M PO_4	7	409 ± 6	0.999
72	6.87	0.05 M PO_4	7	419 ± 18	0.999
72	6.87	0.05 M PO_4	7	404 ± 13	0.999
72	8.74	0.001 M Borax	5	21,300 ± 200	0.999
72	8.72	0.001 M Borax	6	20,200 ± 600	0.999
72	8.89	0.005 M Borax	3	18,800 ± 200	0.999
72	9.09	0.01 M Borax	6	19,400 ± 500	0.999
72	9.06	0.01 M Borax	3	19,600 ± 1100	0.999
85	5.67	0.025 M KH_2PO_4	6	261 ± 6	0.999
85	5.67	0.025 M KH_2PO_4	5	265 ± 8	0.999
85	6.79	0.005 M PO_4	7	2840 ± 210	0.996
85	6.79	0.005 M PO_4	6	2870 ± 1300	0.963
85	6.84	0.01 M PO_4	6	2000 ± 130	0.998
85	7.74	0.01025 M Borax + HCl	5	3630 ± 210	0.998
85	7.77	0.01025 M Borax + HCl	5	5950 ± 3960	0.933
85	7.77	0.01025 M Borax + HCl	5	4860 ± 860	0.995
85	9.50	0.005 M Borax	6	114,000 ± 1800	0.999
85	9.54	0.005 M Borax	5	76,600 ± 19,500	0.989
85	9.61	0.01 M Borax	6	107,800 ± 4000	0.999
85	9.63	0.01 M Borax	4	87,500 ± 4300	0.999

85°C the half life of tetryl was only a few minutes. Ten-fold changes in tetryl's starting concentration (2 to 20 mg/L) caused no significant change in first-order rate constants nor was catalysis observed with any of the three buffers used. Constant ionic strength was not adhered to in this kinetic study.

The pseudo first-order rate constants (k_{obs}) found in Table 3 were determined from plots of ln tetryl versus time. Linear regression equations for the data were calculated by a least squares method, which also gave the errors in the pseudo first-order rate constants (k_{obs}) and the correlation coefficients. The rate constants in Table 3 represent a 95 percent confidence interval by use of the "Student T-Test." The correlation coefficients for all but three runs were better than 0.99.

Plots of pH versus log k_{ob}. (Figures 3, 4, and 5) for the hydrolyses of tetryl at 40°, 72°, and 85°C ai traight lines with slopes of 0.98, 0.83, and 0.64, respectively. Since the slope reflects the order of the reaction with respect to hydroxide, it appears that either the mechanism is changing or other reactions are occurring as the temperature increases. However, at the lower temperatures the order appears to approach 1.0. Therefore, with respect to hydrolysis at 40°C, tetryl is characterized by the standard rate expression:

$$-d\ \frac{[tetryl]}{dt} = k[tetryl]\ [OH^-]$$

where in buffered solutions the following equations apply:

$$-d\ \frac{[tetryl]}{dt} = k_{obs}[tetryl]$$

and

$$k_{obs} = k_2[OH^-]$$

It was not possible to extract hydroxyl ion-independent constants for a possible water reaction.

Table 4 lists the observed rate constants (k_{obs}), pH, temperature, hydroxide ion concentration, and the calculated second-order rate constants (k_2). As can be seen, they are not constant, especially at the higher temperatures. At 40°C the average value for k_2 = 1754 ± 430 $M^{-1}\ hr^{-1}$. There does not appear to be an increasing or decreasing trend in the five values at 40°C. Due to the long duration (> month) of these kinetic runs no further experiments were conducted at this temperature. Based on the available data (Figures 3, 4, and 5), the rate of tetryl hydrolysis is first order in tetryl concentration over the entire temperature range (40° to 85°C) but less than first order in hydroxide ion concentration at 72° and 85°C (see falloff in k_2 values with increase in pH--Table 4). This suggests a possible competing reaction where tetryl is disappearing by a route which does not depend on hydroxide ion concentration. Evidence for a thermal first-order decomposition of tetryl is discussed below. The scope of this task did not permit further investigation of possible side reactions.
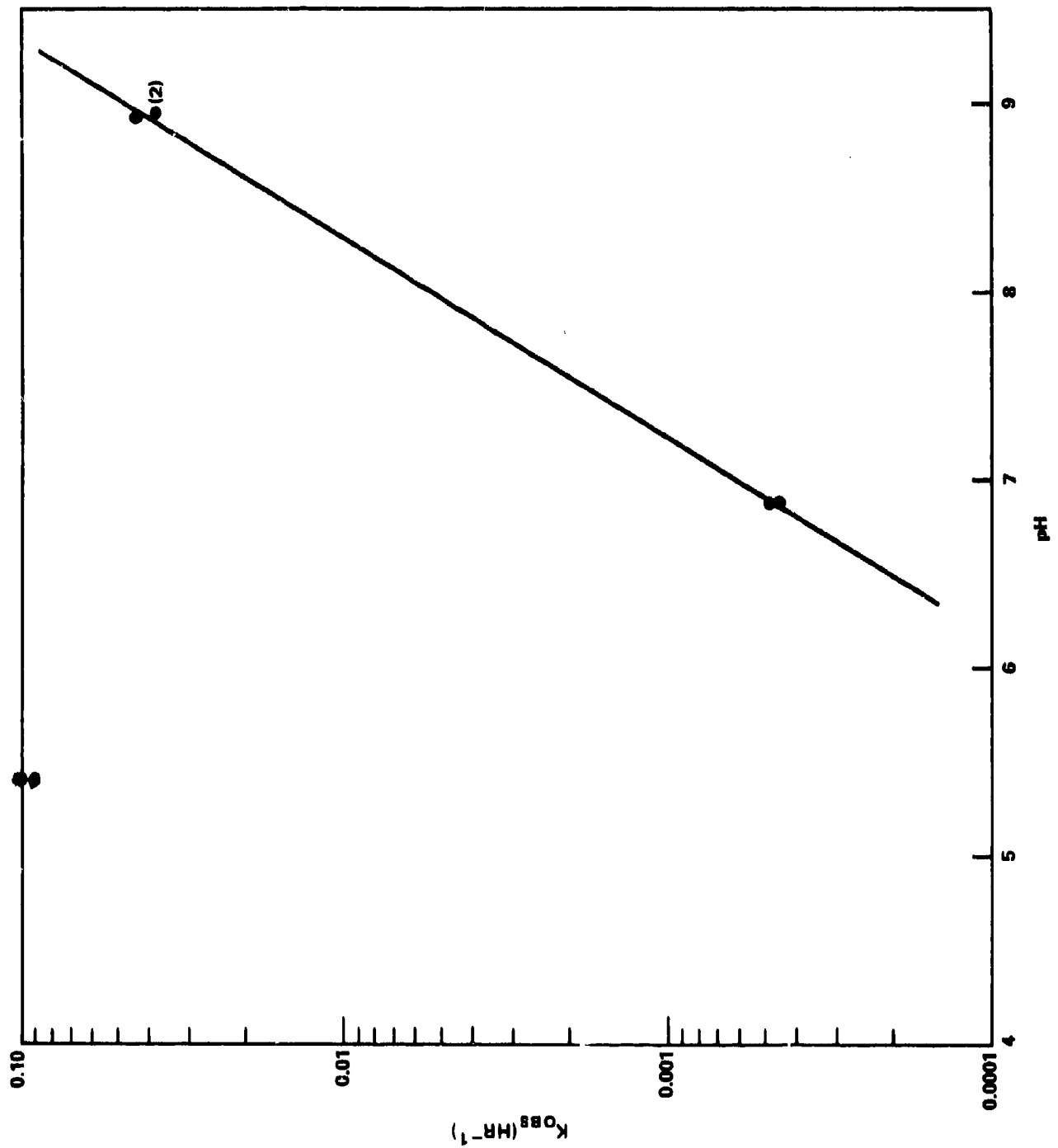
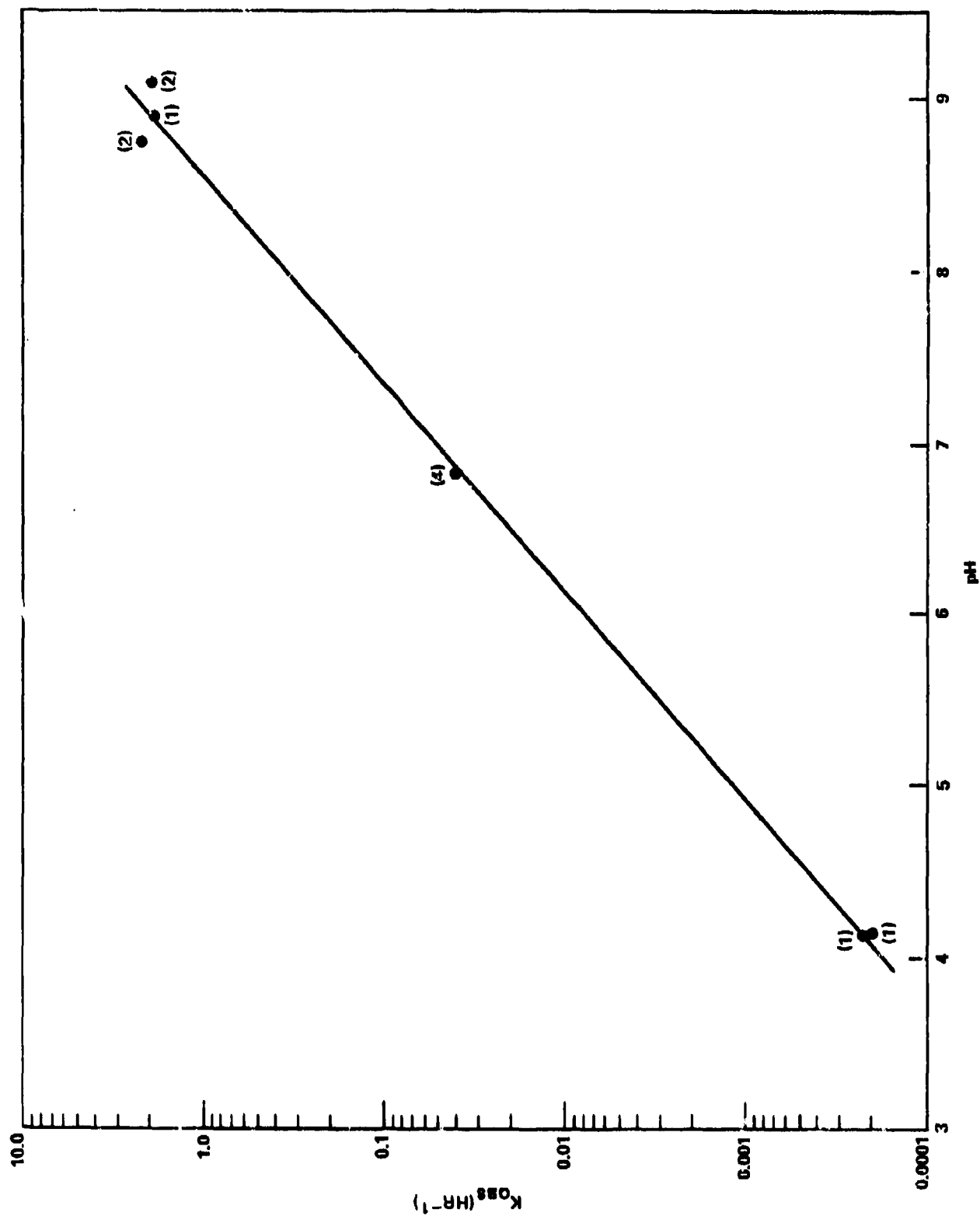FIGURE 3. 40°C TETRYL HYDROLYSIS RATES AT VARIOUS pH VALUES

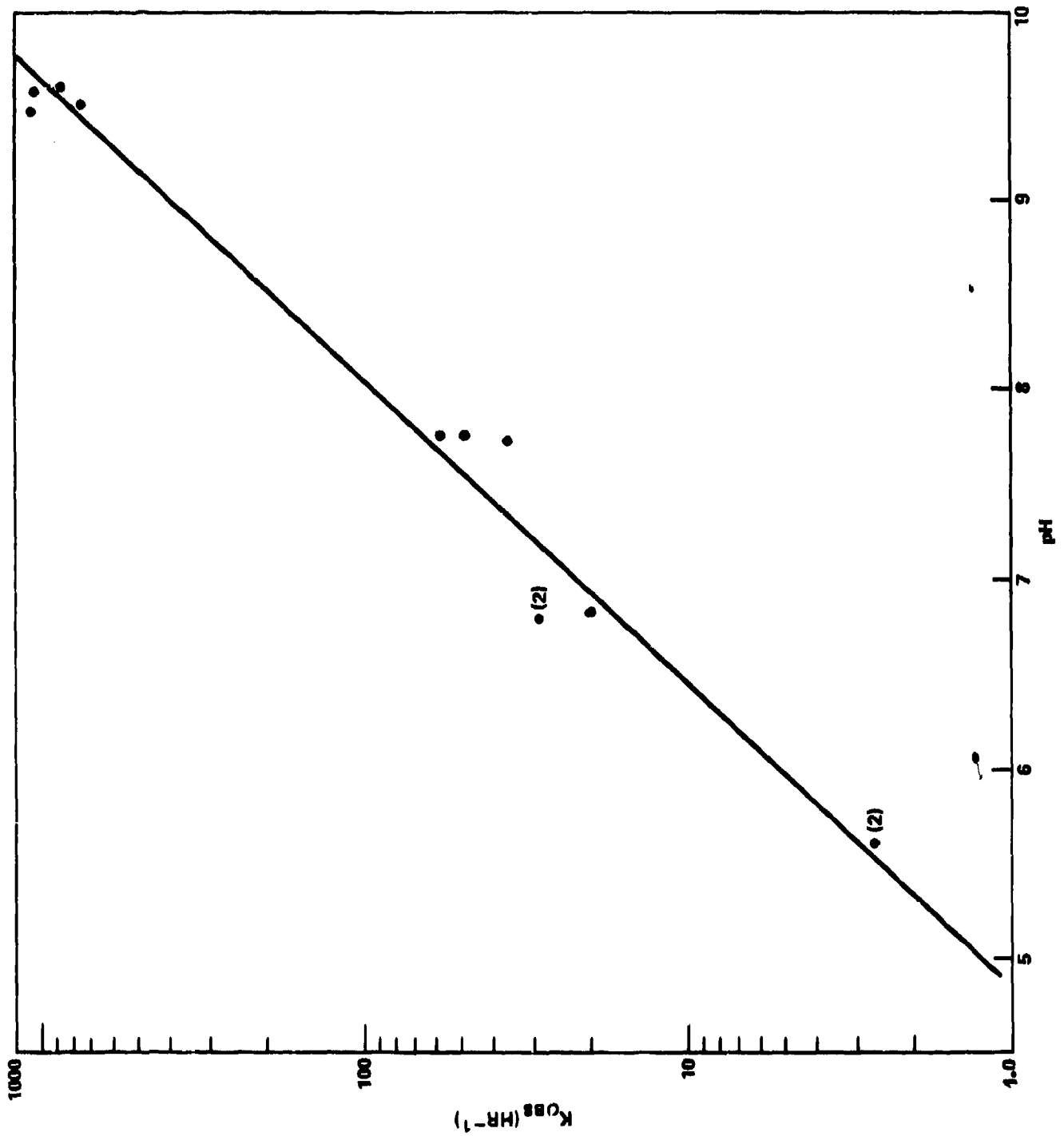FIGURE 4. 72°C TETRYL HYDROLYSIS RATES AT VARIOUS pH VALUES

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FIGURE 5. 85°C TETRYL HYDROLYSIS RATES AT VARIOUS pH VALUES

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TABLE 4. KINETIC DATA OF TETRYL HYDROLYSIS IN BUFFERED AQUEOUS SOLUTIONS

TEMP (°C)	pH	$k_{obs}(hr^{-1})$	$k_2(M^{-1}hr^{-1}) = k_{obs}/[OH^-]$	OH^- CONCENTRATION (MOLES/LITER)
40	6.88	0.000453	1,805	2.51×10^{-7}
40	6.88	0.000493	1,964	2.51×10^{-7}
40	8.94	0.0446	1,546	2.88×10^{-5}
40	8.96	0.0388	1,285	3.02×10^{-5}
40	8.96	0.0437	1,447	3.02×10^{-5}
72	4.13	0.000201	89,732	2.24×10^{-9}
72	4.13	0.000243	108,482	2.24×10^{-9}
72	6.87	0.0401	32,602	1.23×10^{-6}
72	6.87	0.0409	33,252	1.23×10^{-6}
72	6.87	0.0419	34,065	1.23×10^{-6}
72	6.87	0.0404	32,845	1.23×10^{-6}
72	8.72	2.02	23,192	8.71×10^{-5}
72	8.74	2.13	23,355	9.12×10^{-5}
72	8.89	1.88	14,687	1.28×10^{-4}
72	9.06	1.96	10,262	1.91×10^{-4}
72	9.09	1.94	9,509	2.04×10^{-4}
85	5.67	0.0261	185,000	1.41×10^{-7}
85	5.67	0.0265	188,000	1.41×10^{-7}
85	6.79	0.284	153,000	1.86×10^{-6}
85	6.79	0.287	154,000	1.86×10^{-6}
85	6.84	0.200	96,000	2.09×10^{-6}
85	7.74	0.363	22,000	1.66×10^{-5}
85	7.77	0.595	33,000	1.78×10^{-5}
85	7.77	0.486	27,000	1.78×10^{-5}
85	9.50	11.40	12,000	9.54×10^{-4}
85	9.54	7.66	7,300	1.05×10^{-3}
85	9.61	10.78	8,800	1.23×10^{-3}
85	9.63	8.75	6,600	1.29×10^{-3}

Values of $[OH^-]$ are calculated from the expression, $\log[OH^-] = pH + \log k_w$ where $\log k_w = -13.482$; -12.776; and -12.523 at 40°, 72°, and 85°C, respectively.[11]

Attempts to extract a first-order thermal decomposition rate from the 72° and 85°C rate data were unsuccessful. This suggests a more complicated breakdown of tetryl at higher temperatures. The results of the second-order rate data (Table 4) also preclude a good Arrhenius plot, which would have allowed an accurate prediction of the hydrolysis rates under environmental conditions. In lieu of that, however, the hydrolysis rates at 40°C and pH 6.8 ($t_{1/2}$ = 63 days) give an indication of what tetryl's half life will be under environmental conditions. Assuming that the measured first-order hydrolysis rate constant (k_{obs}) changes by a factor of two for each 10°C change in temperature, the $t_{1/2}$ at 20°C and pH 6.8 would be 254 days. This "rule of thumb" is based on an hydrolysis activation energy (E_h) of about 18 Kcal/mole. Since the values of $E_{h\ max}$ range from 15 to 28 Kcal/mole, the rate constant over this range can vary by a factor of 1.8 to 3.0 for every 10°C change. Therefore, the extrapolated rate constant is only semiquantitatively correct. Based on the E_h range, the $t_{1/2}$ range would be 302 ± 76 days for tetryl hydrolysis at 20°C and a pH of 6.8.

CONCLUSIONS AND RECOMMENDATIONS

Although the environmental hydrolysis half life of tetryl ($t_{1/2} \cong 302 \pm$ 76 days) could only be estimated for a range of activation energies, we consider this to be a realistic value for 20°C and pH 6.8. It should be kept in mind, however, that some soils[12] might have a strong accelerating effect on tetryl's hydrolysis rate which could drastically alter its environmental hydrolysis half life. The question of the formation of the potentially toxic methylnitramine under environmental conditions should be investigated. Methylnitramine formation was observed to be less than 5 percent in the light hydrolysis reactions but to be greater than 50 percent in the higher pH dark hydrolysis reaction. The relative hydrolysis rate of methylnitramine compared to tetryl has not been determined. Additional experiments are also needed to determine the unidentified products formed in these reactions.

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